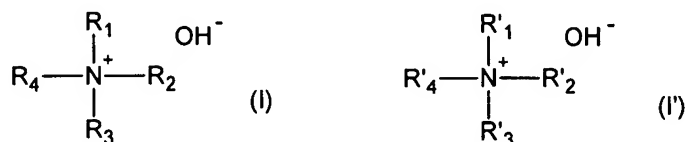


CLAIMS

1. A catanionic membrane in the form of an organized solid bilayer comprising a lateral alternation of anionic surfactants with  $H^+$  counterions and of cationic surfactants with cocrystallized  $OH^-$  counterions in which the mole fraction (MF): molar amount of anionic surfactants ( $Q_{AS}$ )/(molar amount of anionic surfactants ( $Q_{AS}$ ) + molar amount of cationic surfactants ( $Q_{CS}$ )) is greater than 0.5, said membrane forming a surface that is at least locally flat, characterized in that said bilayer is stabilized with at least one polymer that is neutral and hydrophobic or of overall electrical charge opposite the effective charge of said catanionic membrane, said polymer being adsorbed onto said surface.

2. The membrane as claimed in claim 1, characterized in that the cationic and anionic surfactants are chosen from surfactants with a melting point of greater than  $30^\circ C$ .

3. The membrane as claimed in claim 1 or 2, characterized in that the cationic surfactants are chosen from the monocatenary and bicatenary quaternary ammoniums of formulae (I) and (I'), respectively, below:



in which:

-  $R_1$ ,  $R_2$  and  $R_3$ , which may be identical or different, represent a  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl or  $(C_1$ - $C_4)$ alkyl ether radical,

-  $R'_1$  and  $R'_2$ , which may be identical or different, represent a  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl or  $(C_1$ - $C_4)$ alkyl ether radical,

-  $R'_3$  and  $R'_4$ , which may be identical or different, represent a saturated or unsaturated  $C_8$ - $C_{24}$

hydrocarbon-based chain, a benzyl or (C<sub>4</sub>-C<sub>20</sub>)alkylbenzyl radical or a (C<sub>4</sub>-C<sub>20</sub>)alkyl ester group,

- R<sub>4</sub> represents a saturated or unsaturated C<sub>8</sub>-C<sub>24</sub> hydrocarbon-based chain, a benzyl or  
5 (C<sub>4</sub>-C<sub>20</sub>)alkylbenzyl radical or a (C<sub>4</sub>-C<sub>20</sub>)alkyl ester group;  
and mixtures thereof.

4. The membrane as claimed in claim 3,  
characterized in that the C<sub>1</sub>-C<sub>4</sub> alkyl radicals are  
10 methyl radicals.

5. The membrane as claimed in claim 3 or 4,  
characterized in that the compounds of formula (I) are  
chosen from cetyltrimethylammonium hydroxide, dodecyl-  
trimethylammonium hydroxide, stearyltrimethylammonium  
15 hydroxide, tetradecyltrimethylammonium hydroxide,  
N-(2-carboxyethyl)-N,N-dimethyl-1-hexadecanaminium  
hydroxide, N-(2-hydroxyethyl)-N,N-dimethyl-1-hexa-  
decanaminium hydroxide, cetyltriethylammonium  
hydroxide, dodecyltriethylammonium hydroxide,  
20 stearyltriethylammonium hydroxide, tetradecyl-  
triethylammonium hydroxide, cetyltripropylammonium  
hydroxide, dodecyltripropylammonium hydroxide,  
stearyltripropylammonium hydroxide and  
tetradecyltripropylammonium hydroxide.

25 6. The membrane as claimed in claim 3 or 4,  
characterized in that the compounds of formula (I') are  
chosen from didodecyldimethylammonium hydroxide,  
didodecyldiethylammonium hydroxide, didodecyldipropyl-  
ammonium hydroxide, didodecyldibutylammonium hydroxide  
30 and dicetyldimethyltrimethylammonium hydroxide.

7. The membrane as claimed in any one of  
the preceding claims, characterized in that the anionic  
surfactants are chosen from carboxylic acids with a  
C<sub>8</sub>-C<sub>24</sub> carbon-based hydrophobic chain with H<sup>+</sup> counter-  
35 ions and phosphates and sulfonates with H<sup>+</sup> counterions  
comprising one or two C<sub>12</sub>-C<sub>20</sub> alkyl chains.

8. The membrane as claimed in claim 7,  
characterized in that the anionic surfactants are  
chosen from myristic acid, lauric acid and palmitic

acid, phosphates, sulfates, benzyl sulfates and monocatenary glycerol monoesters.

9. The membrane as claimed in any one of claims 3 to 8, characterized in that the bilayers  
5 consist:

a) either of a cationic surfactant of formula (I) as defined in claim 3 and in which the radicals  $R_1$ ,  $R_2$  and  $R_3$  are identical and represent a methyl radical and  $R_4$  represents a hydrocarbon-based chain containing  
10 X carbon atoms, X being between 8 and 24 inclusive, combined with a carboxylic acid as defined in claim 6 in which the  $C_8$ - $C_{24}$  carbon-based hydrophobic chain contains  $X \pm 4$  carbon atoms;

b) or of a cationic surfactant of formula (I') as defined in claim 3 in which the radicals  $R'_1$  and  $R'_2$  are identical and represent a methyl radical and  $R'_3$  and  $R'_4$  are identical and represent a hydrocarbon-based chain containing X carbon atoms, X  
15 being between 8 and 24 inclusive, combined with a carboxylic acid as defined in claim 6 in which the  $C_8$ - $C_{24}$  carbon-based hydrophobic chain contains  $X \pm 4$  carbon atoms;

c) or a phosphate or a sulfonate comprising two identical alkyl chains containing X carbon atoms, X  
25 being between 8 and 24 inclusive, combined with a cationic surfactant of formula (I) as defined in claim 3 and in which the radicals  $R_1$ ,  $R_2$  and  $R_3$  are identical and represent a methyl radical and  $R_4$  represents a  $C_8$ - $C_{24}$  alkyl chain;

d) or a phosphate or a sulfonate comprising only one alkyl chain containing X carbon atoms, X being  
30 between 8 and 24 inclusive, combined with a cationic surfactant of formula (I') as defined in claim 3 and in which the radicals  $R'_1$  and  $R'_2$  are identical and represent a methyl radical and  $R'_3$  and  $R'_4$  are identical  
35 and represent a  $C_8$ - $C_{24}$  alkyl chain.

10. The membrane as claimed in claim 9, characterized in that the bilayers are formed from a combination of cetyltrimethylammonium with  $OH^-$

counterions and myristic acid with  $H^+$  counterions.

11. The membrane as claimed in any one of the preceding claims, characterized in that the mole fraction  $Q_{AS}/(Q_{AS} + Q_{CS})$  is between 0.52 and 0.66.

5        12. The membrane as claimed in any one of the preceding claims, characterized in that the bilayers also contain a minor molar amount of anionic surfactants with metal counterions.

10        13. The membrane as claimed in any one of the preceding claims, characterized in that the neutral polymers are nonlipid polymers chosen from polysaccharides, polyethylene glycols, polyoxyethylenes, polyvinylpyrrolidone, polyvinyl alcohols, oxyethylenated diblock polymers, block copolymers based  
15        on ethylene oxide and propylene oxide, and triblock copolymers composed of hydrophilic-hydrophobic-hydrophilic blocks.

20        14. The membrane as claimed in any one of claims 1 to 12, characterized in that the polymers with an overall electrical charge opposite the effective charge of the catanionic membranes are polymers of weakly negative electrical charge chosen from polyacrylates, polymethacrylates, polyethyl  
25        methacrylates, polybutyl methacrylates and polystyrene-sulfonates, said polymers being substituted to more than 75% randomly with neutral water-soluble groups.

30        15. The membrane as claimed in claim 14, characterized in that said polymer is a polyethylene glycol with a molecular mass of between 5000 and 50 000 Da.

16. The membrane as claimed in any one of the preceding claims, characterized in that said polymers represent from 10% to 400% by weight relative to the total weight of the bilayer.

35        17. The membrane as claimed in any one of the preceding claims, characterized in that its mole fraction  $Q_{AS}/(Q_{AS} + Q_{CS})$  is between 0.55 and 0.58 and in that it is in the form of faceted hollow microcrystals.

18. The membrane as claimed in claim 17,

characterized in that it is in the form of hollow polyhedra comprising from 12 to 30 approximately triangular faces.

19. The membrane as claimed in claim 18,  
5 characterized in that it is in the form of hollow icosahedra with an inner volume of between 0.1 and 10  $\mu^3$ .

20. The membrane as claimed in claim 18 or 19, characterized in that, within the organized solid  
10 bilayer of each of the faces of said microcrystals, the lateral alternation of the cocrystallized anionic and cationic surfactants is hexagonal, the flat part of said faces consisting solely of species containing  $H^+$  or  $OH^-$  counterions in stoichiometric amounts, whereas  
15 the apices of said faces are in the form of an internal semitorus predominantly formed from the anionic species in excess and in an amount sufficient to obtain an MF  $Q_{AS}/(Q_{AS} + Q_{CS})$  of between 0.55 and 0.58.

21. The membrane as claimed in claim 20,  
20 characterized in that the apex of each of the faces of a microcrystal forms a pore, together with the apices of the adjacent faces of the same microcrystal.

22. The membrane as claimed in claim 17,  
characterized in that it is in the form of fragments of  
25 hollow polyhedra constituting a stack of three-dimensional catanionic crystals in the form of a "pile of plates".

23. A process for preparing a catanionic membrane as defined in any one of claims 1 to 22, said  
30 process being characterized in that it comprises the following steps:

1) a first step of formation of unilamellar vesicles by mixing, in an aqueous solvent of low conductivity:

- 35 a) a cationic surfactant (CS) with  $OH^-$  counterions in a molar amount  $Q_{CS}$  and  
b) one or more anionic surfactants (AS) in a molar amount  $Q_{AS}$  strictly greater than  $Q_{CS}$ , and corresponding to equations (1)

to (3) below:

$$Q_{AS} = Q_{AS1} + Q_{AS2} \quad (1)$$

$$Q_{AS1} = Q_{CS} \quad (2) \text{ and}$$

$$Q_{AS2} < 2(Q_{CS}) \quad (3)$$

5 in which:

-  $Q_{AS1}$  is the molar amount of an anionic surfactant with  $H^+$  counterions

10 -  $Q_{AS2}$  is the molar amount of an anionic surfactant with  $H^+$  counterions or with metal counterions, said surfactants having a carbon-based chain identical to that of the CS or of the AS with  $H^+$  counterions used in an amount  $Q_{AS1}$ ,

15 said mixture of cationic surfactant and of anionic surfactant being prepared at a temperature above the melting point of the chains of said surfactants;

20 2) a second step of obtaining flat aggregates formed from only one interdigitated or noninterdigitated crystalline molecular bilayer, by cooling the mixture obtained in the first step to a temperature below the melting point of the chains of the surfactants present in the mixture;

25 3) a third step of stabilizing the crystalline molecular bilayers obtained above in the second step, by adding at least one neutral and hydrophobic polymer or a polymer of weakly negative overall electrical charge dissolved in an aqueous solvent of low conductivity, said step being performed  
30 at a temperature below the melting point of the chains of the surfactants present in the mixture.

24. The process as claimed in claim 23, characterized in that, when the excess of anionic surfactant consists of anionic surfactants with metal  
35 counterions, then the first step of the process comprises:

- a first substep in which the cationic surfactant with  $OH^-$  counterions is first mixed with the anionic surfactant with  $H^+$  counterions in an amount  $Q_{AS1}$

equal to  $Q_{CS}$ , and then

- a second substep in which the molar amount  $Q_{AS2}$  of anionic surfactant with metal counterions is then added.

5           25. The process as claimed in claim 23 or 24, characterized in that the aqueous solvents have a conductivity of less than or equal to 1 MOhm.

          26. The process as claimed in any one of claims 23 to 25, characterized in that the aqueous  
10 solvents are chosen from water and glycerol, and mixtures thereof.

          27. The process as claimed in any one of claims 23 to 26, characterized in that, during the first step, the total concentration of surfactants in  
15 the solution is between 0.01% and 3% by weight relative to the total weight of said solution.

          28. The process as claimed in any one of claims 23 to 27, characterized in that, during the first step, the mixture is heated to a temperature of  
20 greater than 30°C and less than 80°C.

          29. The process as claimed in any one of claims 23 to 28, characterized in that, during the first step, at least one active substance is added to the mixture.

25           30. The process as claimed in claim 29, characterized in that the active substance is chosen from pharmaceutical active principles, active substances for cosmetic purposes, cells and DNA or RNA fragments.

30           31. The process as claimed in any one of claims 23 to 30, characterized in that the volume fraction of polymer added to the mixture during the third step is between one and two times the total mass of the cationic and anionic surfactants.

35           32. A catanionic membrane as defined in any one of claims 1 to 22, for use as medicament for the vectorization of active species or for the retention by adsorption and slow diffusion of volatile molecules.

          33. The catanionic membrane as claimed in

claim 32, characterized in that it is in the form of a faceted hollow polyhedron and is used for:

- encapsulating medicaments, for the purpose of vectorizing them,
- 5       - encapsulating whole bacteria or DNA or RNA fragments,
- retaining reagents for chemical reactions taking place inside the polyhedra,
- performing precipitation or crystallization
- 10   reactions inside the polyhedra, by slow diffusion of reagents inside across the pores of the polyhedra,
- as cosmetic ingredient for the manufacture of creams, obtained by flocculation in the form of bunches of polyhedra, and allowing the efficient
- 15   diffusion of active molecules after adsorption of the polyhedron onto surfaces of opposite surface electrical potential.